THE NEAR ULTRA-VIOLET SPECTRA OF BENZENE PART III. FERMI RESONANCE IN THE EMISSION SPECTRUM OF BENZENE

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ABSTRACT. A large number of Fermi doublets have been discovered in the emission spectrum of benzene. These are due to accidental degeneracy in the vibrations 1596 e_g^+ and 1598 e_g^+ (combination of 606 $e_g^+ + 992\ a_{1g}$) further superposed by several quanta of 992 a_{1g} vibration and involving also 923 a_{1g} excited frequency in addition to series of 160 difference frequency. The magnitude of doublet interval with increasing excitation of the vibrations is well represented by an expression derivable from considerations of the first order perturbation in the potential function of the molecule.

INTRODUCTION AND RESULTS

Fermi resonance in the case of benzene seems to have been first discovered by Wilson (1934). The Raman spectrum of benzene shows two strong lines at a frequency difference of 1584 and 1606 instead of one calculated at 1596.* These have been explained as Fermi doublets due to resonance between (1596) e_g^+ and (606 $e_g^+ + 992\ e_{1g} = 1598$) e_g^+.

In the Raman spectrum, lines involving higher vibrational quanta are usually too weak to observe and these vibrations are inactive in the infrared spectrum. Hence Fermi doublets involving overtones or combination tones have not been recorded. In the absorption spectrum similarly only the fundamental Fermi doublet is observed but since absorption can go to different vibrational levels in the excited electronic state, two more doublets have been recorded both of which, however, involve the same fundamental Fermi doublet. In the high pressure fluorescence spectrum (Ingold and Wilson, 1936), there is evidence of not only the fundamental Fermi doublet but also two more doublets involving one and two quanta of 992 superposed on the Fermi doublet.

In the case of the emission spectrum, in addition to the fundamental doublet, four more Fermi doublets are found involving one to four quanta of 992 successively added to both components of the doublet. Each of these is further developed into series involving the 160 difference frequency. Some of them also develop into progressions involving the 923 frequency in the excited state overlapped by the 160 difference frequency. The wavenumbers on these doublets ovserved in the course of an investigation on the emission

* All frequencies are given in wavenumbers in cm^{-1} units.

spectrum of benzene§ are collected together in Table I, in which also the bands observed in absorption and fluorescence are suitably indicated.

The Table shows two parallel series of bands termed α and β which involve these doublets. The fundamental doublet frequencies obtained from the value for the mean of the five bands that occur in the 160 series superposed over the fundamental doublet is 1585 and 1602. Similarly the positions from the ground state of the doublets involving 1 to 4 quanta of 992 are obtained as mean values from the corresponding 160 progressions. These data on observed mean frequencies are given in Table III. They enable us to study the Fermi interaction with increasing quanta of vibrations as in CO_2 or H_2O. It must, however, be remembered that the differences in the present case are obtained from the band head data which are themselves subject to an error of about ± 3 cm^{-1}.

DISCUSSION OF RESULTS

The case of accidental degeneracy here met with falls to a certain extent in the same class as of CO_2, which has been fully worked out by Dennison (1932: 1940) and Adel and Dennison (1933). The interaction is treated as a perturbation brought about by anharmonicity. The first order perturbed energies are obtained by solving the secular determinant $|A^r_s - \lambda W_1 \delta^r_s| = 0$. The roots of this determinant λW_1 furnish the required perturbed energies. The quantity A^r_s is the matrix element of the perturbing function $T_1 + \lambda U_1$. The first order perturbation should give the magnitude of the interaction correctly. This is nearly but not wholly borne out by experiment. The agreement between theory and experiment becomes, however, more complete if the second order perturbation is also employed. A complete theory of Fermi resonance for CO_2 is hence given by Dennison and Adel and Dennison, which is further extended by Darling and Dennison (1940) with suitable alterations to H_2O. The accuracy of experimental data available in both these molecules is superior to that in our experiments on benzene. Here we do not observe the band origins as in CO_2 or H_2O particularly in their infrared data but only band heads. It is, therefore, thought that the first order perturbation alone need be considered. The case of methyl halides which is analogous to CO_2 is in this respect particularly interesting and has been worked out by Adel and Barker (1934). Using only the first order perturbation, they obtain expressions for W_α and W_β which are separations from the unperturbed levels including the constant shift $\frac{\Delta}{2}$ due to the ground level. Thus,

$$W_\alpha = \Delta + \left[\frac{\Delta^2}{4} + \frac{nb^2}{2} \right]^{\frac{1}{2}}$$

§ For details of experimental procedure, etc., refer to the paperon the Emission Spectrum of Benzene in the near ultraviolet Part I of this series.

and $$W_\beta = \Delta - \left[\frac{\Delta^2}{4} + \frac{nb^2}{2} \right]^{\frac{1}{2}}$$

where Δ is the displacement of the calculated frequency from the mean of the observed doublet, b^2 is given by $\left(\frac{\Lambda^2 - \Delta^2}{2} \right)$ where Λ is the doublet separation and n takes values 1, 2...etc., b is a measure of the anharmonicity appearing in the cubic part of the potential function.

In benzene, the fundamental perturbation occurs between the singly excited e_u^+ vibration and the single excited composite vibration 1598 e_u^+ (formed by 992 $a_{1g} + 606\ e_u^+$). In other words, the degeneracy is between two doubly degenerate vibrations. For single excitation, the degeneracy is not removed both and vibrations have the same l value namely 1. In this respect the fundamental degeneracy in benzene differs from that in CO_2 or the methyl halides where the fundamental degeneracy is between a singly excited non-degenerate vibration and a doubly excited degenerate vibration. The l value for the non-degenerate vibration being always 0, only the component having $l=0$ of the doubly excited non-degenerate vibration enters into interaction whereas the component having $l=2$ is unaffected.

The observed excited Fermi doublets in benzene arise on account of superposition of a non-degenerate totally symmetrical vibration which has no influence on the l value. The vibration quantum numbers of the frequencies giving rise to the doublets are shown in Table II. Among such doublets found in CO_2, there are similarly those which arise by superposition of a non-degenerate vibration. These considerations lead us to adopt expressions for W_α and W_β similar to those used by Adel and Barker. The value for the component vibrations thus calculated are given in Table III along with the observed values. The agreement is considered satisfactory.

Note added on January 12, 1949.—

In a recent paper which reached us last month, Garforth and Ingold (1948) have made a detailed analysis of the fluorescence bands of benzene. From a re-examination of the spectrograms and micro-photograms of the bands previously reported by Ingold and Wilson (1936), they have recast the data on band maxima and recorded similar resonance doublets. Although there is some discrepancy in the wavelength data it is satisfactory to find that the doublet separations are exactly identical with those recorded here.

TABLE I

Series* ν_{vac}		Int.**	Series ν_{vac}		Int.
α_0^0	36504††	8	β_0^0	36486††	8
α_0^1	36343+††	4·5	β_0^1	36325+††	5
α_0^2	36182††	2·5	β_0^2	36166††	3
α_0^3	36023††	1	β_0^3	36006††	1·5
α_0^4	35871	1	β_0^4	35848††	0
α_{-1}^0	35517††	5	β_{-1}^0	35492††	7
α_{-1}^1	35356††	3	β_{-1}^1	35330††	4·5
α_{-1}^2	35193††	1	β_{-1}^2	35169††	4·5
α_{-1}^3	35038††	2	β_{-1}^3	35007	1
α_{-1}^4	34877††	·5			
α_{-2}^0	34530††	3	β_{-2}^0	34501††	4·5
α_{-2}^1	34371††	3	β_{-2}^1	34338††	3
α_{-2}^2	34208††	1	β_{-2}^2	34176††	3
α_{-2}^3	34046	1·5	β_{-2}^3	34018††	0
α_{-3}^0	33549	1·5	β_{-3}^0	33512††	3
α_{-3}^1	33384	2·5	β_{-3}^1	33347	0
			β_{-3}^2	33189	0
			β_{-4}^0	32524	1·5
			β_{-4}^1	32351	1
			β_{-4}^2	32210	0
α_{1-1}^0	36442	2	β_{1-1}^0	36421+	3·5
α_{1-1}^1	36276	1	β_{1-1}^1	36257	2
			β_{1-1}^2	36097	2
α_{1-2}^0	35455	3·5	β_{1-2}^0	35425	4(?)
α_{1-2}^1	35393	1	β_{1-2}^1	35264	2(?)
α_1^0	37427	0		—	
α_2^0	38353†	2 (?)			

† These are also present in the absorption spectrum Radle and Beck, (1940).
†† These are also present in the fluorescence spectrum Ingold and Wilson (1936).
* The notation followed is the one given in Part I of the series, namely, negative subscripts for superposition of 992 quanta in the ground state and the superscript denoting the quanta of the difference frequency 160 superposed
** The intensities are those visually estimated relative to the intensity of the strongest band B_0^0 as 10.

The complete table given in Part I of the series gives some more bands as belonging to α and β series but since the assignment is not unique, they are not included in this table.

TABLE II

Doublet No.	V_1 606 e_g^+	V_2 992 a_{1g}	V_3 (1596) e_g^+
I	1	1	0
	0	0	1
II	1	2	0
	0	1	1
III	1	3	0
	0	2	1
IV	1	4	0
	0	3	1
V	1	5	0
	0	4	1

TABLE III

$$\Delta = R - (\nu_2 + \nu_3) = 1593.5 - 1598 = -4.5 \text{ cm}^{-1}$$

$$b^2 = \left\{ \frac{\Lambda^2 \mp \Delta^2}{\quad} \right\} = 134.4$$

$$W_{\alpha\beta} = \Delta \pm \left\{ \frac{\Delta^2}{4} + \frac{nb^2}{2} \right\}^{1/2}$$

Doublet No.	Series	Frequencies observed mean values	Frequencies calculated	Values $W_{\alpha,\beta}$	O−C
I	α_0^0	1585	(1585)	−13	0
	β_0^0	1602	(1602)	+ 4	0
II	α_{-1}^0	2572	2574	−16.3	− 2
	β_{-1}^0	2598	2597	+ 7.3	1
III	α_{-2}^0	3559	3563	−18.9	− 4
	β_{-2}^0	3590	3592	+ 9.9	− 2
IV	α_{-3}^0	4542	4553	−21.1	−11
	β_{-3}^0	4579	4586	+12.1	− 7
V	α_{-4}^0	—	5543	−23	—
	β_{-4}^0	5566	5580	+14	−14

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